Thermal Decomposition of 1-Cyclohexyl-1-methylethyl Peroxypivalate

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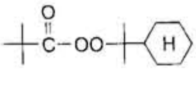
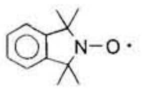
The thermal decomposition of a novel peroxyester, 1-cyclohexyl-1-methylethyl peroxypivalate **1a** in cumene has been studied using the radical trapping technique employing 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl **T**, a stable aminoxyl radical, as the scavenger. Comparable amounts of cyclohexyl radicals and *t*-butyl radicals were generated from the thermolysis of **1a**. Thus, 1-cyclohexyl-1-methylethoxyl radicals **2a** undergo β-scission exclusively. The efficiency of radical generation for **1a** was determined to be 0.56, which is slightly higher than that for *t*-butyl peroxypivalate (0.53).

Peroxyesters are among the most commonly used initiators for the radical polymerization of olefinic compounds such as vinyl chloride and methyl methacrylate.[1] They can also be useful radical sources for kinetic studies in general free radical chemistry.[2,3] Thus, they have both industrial and scientific importance. Recently we have developed a novel peroxyester, 1-cyclohexyl-1-methylethyl peroxypivalate **1a**,[4] which is now commercially available.

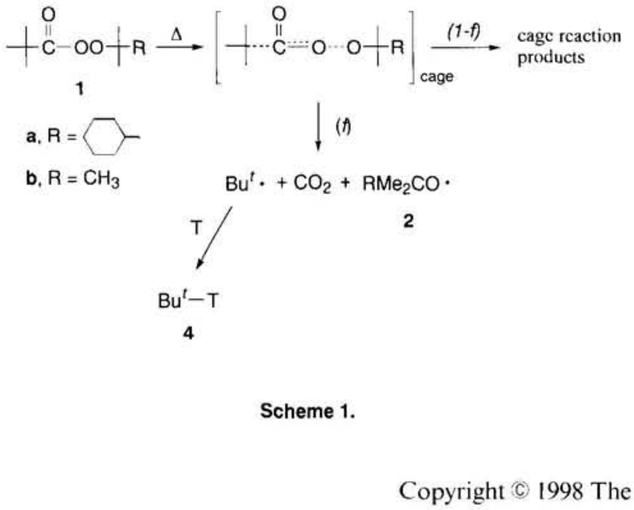


1a



T

t-Alkyl peroxypivalates **1** are known to generate an equimolar amount of *t*-butyl and *t*-alkoxyl radicals **2** via a concerted two-bond scission accompanied by a cage reaction in a solvent, such as cumene (Scheme 1).[5] In the case of **1a**, β-scission of the corresponding *t*-alkoxyl radicals, 1-cyclohexyl-1-methylethoxyl radicals **2a** (R = $C_6H_{11}^{cyclo}$ in **2**), to form cyclohexyl radicals is of interest. There have been no previous reports regarding this reaction.



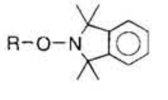
Scheme 1.

This letter reports the thermolysis of the peroxyester **1a** with respect to the extent of β-scission of **2a** and the efficiency of radical generation (*f*) for **1**. The value of *f* is important from the viewpoint of it's practical use as a polymerization initiator. In this study, the radical trapping technique employing 1,1,3,3-tetramethyl-2,3-dihydro-1*H*-isoindol-2-yloxyl **T** has been used. This technique is based on the fact that **T** reacts with carbon-centred radicals at close to diffusion controlled rates to produce stable alkoxyamines, but does not react with oxygen-centred radicals.[6] We have shown in a previous paper that **T** does not influence the thermal decomposition of **1**.[3a]

Peroxypivalate **1a** was prepared by the reaction of pivaloyl chloride with 1-cyclohexyl-1-methylethyl hydroperoxide **3**[7] (95.0% purity) in alkaline solution according to the literature procedure reported for the preparation of 1,1,2,2-tetramethylpropyl peroxypivalate.[8] The structure of **1a** was consistent with it's NMR and IR spectra,[9] and the purity, determined by iodometric titration, was 98.5%.

The thermolysis of **1a** (0.10 mol dm^{-3}) was carried out in cumene at several temperatures. It was measured by monitoring the concentration of **1a** by iodometric titration with time. The rate of decomposition was found to satisfy first-order kinetics at all of the temperatures with rate constants: 0.356, 1.57, 5.72 and 20.0 × 10^{-5} s^{-1} at 40, 50, 60 and 70 °C respectively. The half-life for the thermolysis of **1a** in cumene is 3.4 h at 60 °C, which is about half the value for the *t*-butyl analogue (R = Me in **1**, the half-life is 7.2 h at 60 °C).[3a]

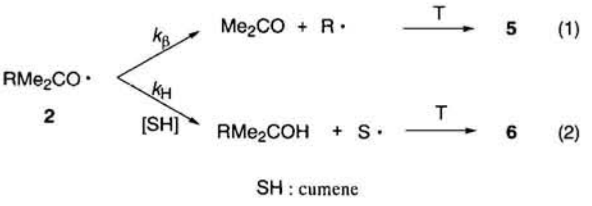
The decomposition mechanism of **1a** was studied using the radical trapping technique. Following the thermolysis of **1a** (0.040 mol dm^{-3}) in cumene at 60 °C for 1 h and in the presence of excess of **T**, alkoxyamines as the reaction products were isolated by preparative HPLC and characterized by HPLC-MS and NMR. Alkoxyamines **4**,[3a] **5a**[10] and **6**[8] were formed.



5a : R = $C_6H_{11}^{cyclo}$
5b : R = Me
6 : R = CMe_2Ph

The yields of **5a** and **6** were 96.8% and 0.6% relative to **4**. *t*-Butyl radicals generated in the thermolysis were immediately trapped by **T** to form *t*-butoxyamine **4** (see Scheme 1). On the other hand, 1-cyclohexyl-1-methylethoxyl radicals **2a** underwent β-scission, generating cyclohexyl radicals (to form **5a**), and hydrogen abstraction, generating cumyl radicals (to form **6**) (eqs 1 and 2 in Scheme 2). The comparable yields of **5a** and **4** indicate that β-scission of **2a** competes effectively with abstraction.

In an analogous experiment with **1b** (R = Me in **1**), and in contrast to **1a**, the corresponding product derived from *t*-butoxyl radicals **2b** (R = Me in **2**), i.e. methoxyamine **5b**,[3a] was

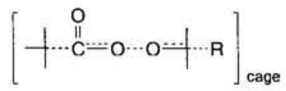


Scheme 2.

observed as a very minor product (1.7% relative to **4**) and the main product derived from **2b** was alkoxyamine **6** (94.0% relative to **4**), formed by hydrogen abstraction.

Taking the concentration of solvent as [SH] = 7 mol dm^{-3}, the values of k_β/k_H for **2a** and **2b** at 60 °C are 1.1×10^3 and 0.4×10^{-1} mol dm^{-3} respectively. If k_H is assumed to have the similar values for any alkoxyl radical as has been suggested[11] (k_H = ca. 10^6 dm^3 mol^{-1} s^{-1}),[12] the values of k_β for **2a** and **2b** can be estimated to be ca. 10^9 and ca. 4×10^4 s^{-1} respectively, indicating the vastly different behavior of alkoxyl radicals **2a** and **2b**. This can be attributed to the stability of the alkyl radicals formed.[13]

The radical generation efficiency (*f*) for **1a** and **1b** was also measured by a trapping experiment. When peroxyester **1** (0.050 mol dm^{-3}) in cumene was completely decomposed at 60 °C for 72 h (> 10 half-lives) in the presence of excess of **T** (0.110 mol dm^{-3}), the value of *f*, determined from the yield of *t*-butoxyamine based on peroxyester consumed, is 0.56 for **1a** and 0.53 for **1b**. The observed value for **1b** is close to that given in previous reports, in which the extent of the cage reaction (1-*f*) for **1b** in cumene was estimated to be ca. 0.50.[5b,d] It is interesting to note that the efficiency for **1a** is similar to that for **1b** despite the very different behaviour of the two alkoxyl radicals. This result suggests that in the previously proposed[5d] transition state, **7**, for the thermal decomposition of peroxypivalates, the extent of β-scission is probably quite small. If the extent of C-R (R = cyclohexyl) bond cleavage is advanced in the transition state, the radical efficiency for **1a** must be increased correspondingly because the reaction of the caged radicals is hindered by intervening two molecular fragments (i.e. CO_2 and acetone), which allow more of the radicals to escape.[14]



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In summary, we have found that **1a** is a low temperature active organic peroxide and that *t*-alkoxyl radicals **2a** undergo very fast β-scission to generate cyclohexyl radicals. Thus, in contrast to **1b**, the thermolysis of **1a** generates alkyl radicals exclusively. This indicates that **1a** is expected to be a very useful polymerization initiator for monomers such as methyl methacrylate because alkyl radical initiation proceeds exclusively by addition.[3] Thus the formation of unsaturated end groups in the resulting polymer by abstraction is minimized. Further, **1a** can be used as a convenient source of cyclohexyl radicals, which in previous work have been generated from the reaction of cyclohexylmercury salt with $NaBH_4$.[15]

A study of the initiation mechanism of **1a** in the radical polymerization of monomers such as methyl methacrylate is in progress. The reactivity of cyclohexyl radicals towards addition to various monomers will also be studied.

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7 Peroxide **3** was prepared from the reaction of 1-cyclohexyl-1-methylethanol with 50% H_2O_2 in the presence of 98% H_2SO_4. Spectroscopic data of **3**; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 0.85-1.85 (11H, m, C_6H_{11}), 1.12 (6H, s, Me); ^{13}C NMR ($CDCl_3$) δ = 21.5, 26.6, 26.7, 27.6, 44.5, 85.2; IR (neat), 3400, 2990, 2930, 2860, 1450, 1370, 1260, 1240, 1210, 1180, 1150, 1120, 1040, 890, 860, 840, 820, 800 and 750 cm^{-1}.

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9 Spectroscopic data of **1a**; ^{1}H NMR (200MHz, $CDCl_3$) δ = 0.88-1.86 (11H, m, C_6H_{11}), 1.20 (6H, s, Me) and 1.23 (9H, s, Bu^t); ^{13}C NMR ($CDCl_3$) δ = 21.8, 26.5, 26.7, 27.3, 27.5, 38.9, 45.4, 87.8 and 175.0; IR (neat) 2950, 2900, 2810, 1760, 1480, 1450, 1380, 1360, 1250, 1090, 1020, 880, 850 and 750 cm^{-1}.

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